

Replacing “OR” Logic and Mass Accuracy with “AND/OR” Logic and Mass Resolving Power, as the Basis for Peak Assignment in Top-Down Mass Spectrometry Data.

Wednesday, August 27, 2025 3:10 PM (20 minutes)

This talk concerns how to assign a peak in a fragment ion mass spectrum to a polypeptide sequence. This task is recognized to be problematic for some internal fragment ions, and as we will show, is problematic for all ion types (e.g., terminal fragments). Most experimental mass (peak) to theoretical database entry (molecule) correlations are delivered as a byproduct of automated peptide/proteoform-spectral (PSM) matches. Unfortunately, peak assignments are not what PSMs were designed to do. There are conditions where it is fair to assume—as many do—that PSM peak assignments are correct. We show these conditions involve sparsely populated experimental data generated, for example, with prior MS technology. We propose and demonstrate that assigning fragments ions from rich, e.g., modern, mass spectra, including from TDMS, requires changing the search paradigm from “OR” to “AND/OR” logic for assigning a given peak to related database entries, as well as moving from the use of mass accuracy-related search space to a mass resolution-related search space.

User consent

yes

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